PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the Production of Filaments, Films and like shaped articles from Acrylonitrile Polymers

We, BRITISH CELANESE LIMITED, a British Company, of Cellanese House, 22/23, Hanover Square, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of filaments, films and like shaped articles from solutions of polyacrylonitrile or of copolymers containing acrylonitrile as the major constituent.

According to the invention a solution of a fibre-forming polyacrylonitrile or of a fibre-forming copolymer containing a preponderating proportion of acrylonitrile is shaped, as by extrusion or casting, and is set by means of a coagulating medium comprising as the chief or sole constituent a liquid aromatic hydrocarbon or a liquid halogenated aliphatic hydrocarbon.

The invention is of particular importance in the production of the shaped articles from polyacrylonitrile itself. It is however also of value in connection with copolymers, especially copolymers of acrylonitrile and another vinyl compound or compounds, in which acrylonitrile is the preponderating constituent, and especially in which the proportion of acrylonitrile exceeds 85%. Examples of vinyl compounds which may be copolymerised with acrylonitrile are methacrylonitrile, vinyl chloride, vinyl acetate, acrylic acid esters such as methyl and phenyl acrylate, styrene and its derivatives, and vinylidene chloride. For the sake of brevity the term "acrylonitrile polymers" will be employed to denote both polyacrylonitrile itself and copolymers in which acrylonitrile preponderates.

Of the two classes of coagulating medium specified, we prefer to use the aromatic hydrocarbons, especially benzene, toluene, the xylenes, and mixtures of alkyl benzenes such as solvent naphtha. However, good results are also obtainable using halogenated aliphatic hydrocarbons, preferably chlorinated paraffins, especially such as have a symmetrical structure such as carbon tetrachloride, ethylene di-chloride and symmetrical tetrachlorethane. The hydrocarbon or halogenated hydrocarbon may if desired be employed mixed with a smaller proportion of a more highly polar liquid, e.g. an alcohol such as ethyl alcohol. Preferably the proportion by volume of a more polar liquid in the coagulating medium does not exceed 30% or the limit of miscibility with the aromatic hydrocarbon or halogenated aliphatic hydrocarbon, whichever is the lower.

Various solvents are available for forming solutions of the acrylonitrile polymers to be used in the process of the invention, for example dimethyl formamide, gamma-butyrolactone, gamma and delta-valerolactones, propiolactone and other beta-lactones, sulpholane (tetramethylene cyclic sulphone), and solvents comprising nitromethane with or without formic acid. Mixtures of two or more solvents may be used. Of these solvents we prefer to use dimethyl formamide or a homogeneous mixture of nitromethane and water containing at least 6% of water, but less water than nitromethane.

The acrylonitrile polymer preferably has a viscosity between 2.5 and 4 centistokes, and especially between about 2.5 and 3.5 centistokes. (Here and throughout this specification the viscosities of the polymers are expressed in terms of the viscosity of a 1% solution of the polymer in dimethyl formamide at 20° C.) The concentration of the solution to be extruded or cast may be between 7.5% and 25%, and its temperature should be kept sufficiently high to ensure that the polymer does not begin to separate before the extrusion or casting. Moreover the temperature and the concentration of the solution should be correlated with the viscosity of the polymer to give a solution of satisfactory viscosity for extruding or casting. For example when using a 20% solution in dimethyl formamide of a polyacrylonitrile of viscosity about 2.5 centistokes, it is usually desirable to keep its temperature above about 40° C. Other solutions may require to be kept at or above higher minimum temperatures. The coagulating medium may be at or below room temperature, say at 10°—20° C., but is preferably at a temperature above 50° C. Temperatures between 55° and 100°

C. are particularly advantageous; when using such high temperatures, the coagulating agent should of course be so chosen that the desired operating temperature is no higher than its boiling point, and is preferably somewhat below it.

The invention may be applied to the manufacture of films and like shaped articles by extrusion or casting methods, but is particularly important in connection with the manufacture of filaments from the acrylonitrile polymers. (The term "filaments" is employed to denote filamentary material in general, for example multi-filament twisted and untwisted yarns, tow, and single continuous filaments of high denier.) The filaments may be made by extruding the solution of the polymer through appropriate orifices, horizontally or vertically, or at an angle to the horizontal, into a bath of the desired coagulating medium; the coagulating medium may flow in the same direction as, or in the opposite direction or more or less transversely to, the direction of travel of the filaments, or it may be relatively quiescent.

Filaments, films, and like shaped articles made in accordance with the invention may be subjected to subsequent stretching, setting, and relaxing operations such as are known for filaments or films of polyacrylonitrile made by other methods. For example they may be stretched in hot water, e.g. water at a temperature between 80° and 100° C., or while softened by dry heat, e.g. while passing over a heated metal surface at a temperature of about 120°—150° C. Thus filaments may be stretched for example to about 5—15 times their original length.

The stretched filaments and films may be "relaxed" in order to increase their extensibility, for example by heating them to about 140°—200° C. in the absence of tension or under a tension insufficient to prevent them shrinking. Moreover filaments and films made in accordance with the invention, whether or not they have been stretched, may be "set" by heating them for instance to a temperature between 100° and 160° C. while they are held at constant length in order to increase their dimensional stability. For example filaments may be heated while passing round a thread-storage thread-advancing reel or like device.

The following examples illustrate the invention.

EXAMPLE 1.

A 20% solution in dimethyl formamide of a polyacrylonitrile of viscosity 2.52 centistokes was extruded in the form of filaments while at a temperature of 40° C. into a coagulating bath of benzene or of a 5:1 (by volume) mixture of benzene and ethyl alcohol at a temperature of about 60° C. The filaments produced were of good strength and lustre. The same solution was also spun with a coagulating bath temperature of 10°—20° C.

EXAMPLE 2.

A 20% solution in dimethyl formamide of a polyacrylonitrile of viscosity 3.0 centistokes was extruded at a temperature of 70° C. in the form of filaments into a coagulating bath of benzene or toluene at 65° C. The filaments obtained were passed over a heated metal surface at 140°—150° C. and stretched to 10 times their original length. They were then heated to 140° C. in the absence of tension, whereupon they shrank to 85% of their stretched length. Before this relaxing operation the stretched filaments had a tenacity of 2.2 grams per denier, and an extensibility of 6%; after relaxation the tenacity was 2.0 grams per denier, and the extensibility was 12%.

EXAMPLE 3.

Polyacrylonitrile of viscosity 3.3 centistokes was heated with nitromethane to 85° C., and sufficient water, also at 85° C., was mixed in to give a mixture comprising 9 parts by volume of nitromethane and 1 part by volume of water. The mixture was then stirred until it formed a clear solution. This solution, still at 85° C., was extruded in the form of filaments into a coagulating bath of xylene (a commercial mixture of the isomers) at about the same temperature. The filaments were at once stretched to 8 times their length while passing over a metal plate heated to 140° C., after which they were set by being heated at constant length to 140° C. The product had a good tenacity and good dimensional stability.

EXAMPLE 4.

The process of Example 3 was repeated except that the polyacrylonitrile was dissolved in a mixture of 3 volumes of nitromethane to 1 volume of aqueous formic acid of concentration 85%.

EXAMPLE 5.

Polyacrylonitrile of viscosity 3.3 centistokes was dissolved in a mixture of nitromethane and water containing 92% by weight of nitromethane and 8% by weight of water to form a solution of concentration 10%. This solution was extruded at a temperature of about 80° C. into a bath of solvent naphtha at 80°—85° C. The filaments produced were stretched to 5 times their original length while passing through an air bath at 180° C.

EXAMPLE 6.

The solution employed in Example 2 was extruded at a temperature of 70° C. into a coagulating bath of carbon tetrachloride or ethylene dichloride at the same temperature, and the resulting filaments stretched by 5

times their length while passing over a metal surface heated to 140° C.

While the above examples all deal with the production of filaments from polyacrylonitrile, similar conditions can be used for the production of films and foils. The polyacrylonitrile can be replaced by another acrylonitrile polymer, especially a fibre-forming copolymer of acrylonitrile and vinyl acetate, vinyl chloride or methyl acrylate containing 85—95% of acrylonitrile.

What we claim is:—

1. Process for the manufacture of filaments, films and like shaped articles having a basis of a fibre-forming acylonitrile polymer (as hereinbefore defined), which comprises shaping a solution of the polymer and setting it by means of a coagulating medium comprising as the chief or sole constituent a liquid aromatic hydrocarbon or a liquid halogenated aliphatic hydrocarbon.

2. Process according to Claim 1, wherein the coagulating medium comprises benzene, toluene, xylene or a mixture of two or more of these compounds.

3. Process according to Claim 1, wherein the coagulating medium comprises a chlorinated paraffin hydrocarbon.

4. Process according to Claim 1, wherein the coagulating medium comprises carbon tetrachloride, ethylene dichloride or symmetrical tetrachlorethane.

5. Process according to any of the preceding claims, wherein the coagulating medium contains, besides the aromatic hydrocarbon or halogenated aliphatic hydrocarbon, up to 30% by volume of a more highly polar compound which in the proportion present is miscible with the aromatic hydrocarbon or halogenated aliphatic hydrocarbon.

6. Process according to any of the preceding claims, wherein the coagulating medium is at a temperature above 50° C.

7. Process according to any of the preceding claims, wherein the acrylonitrile polymer is in solution in dimethyl formamide or in a homogeneous mixture of nitromethane and water containing at least 6% of water but less water than nitromethane.

8. Process according to any of the preceding claims, wherein the acrylonitrile polymer is polyacrylonitrile.

9. Process according to any of the preceding claims, wherein continuous filaments are formed.

10. Process for the manufacture of filaments, films and like shaped articles having a basis of a fibre-forming acrylonitrile polymer (as hereinbefore defined) substantially as described.

11. Filaments, films and like shaped articles having a basis of a fibre-forming accrylonitrile polymer (as hereinbefore defined) and obtained by the process of any of the preceding claims.

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PROVISIONAL SPECIFICATION

Improvements in the Production of Filaments, Films and like shaped articles from Acrylonitrile Polymers

We, BRITISH CELANESE LIMITED, a British Company, of Cellanese House, 22/23, Hanover Square, London, W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to the production of filaments, films and like shaped articles from solutions of polyacrylonitrile and copolymers containing acrylonitrile as the major constituent.

According to the invention, a solution of a fibre-forming polyacrylonitrile or copolymer containing 85% or more of acrylonitrile is extruded or cast into a desired form and is set by means of a coagulating medium comprising as the chief or sole constituent an organic liquid of low or zero dipole moment, especially of dipole moment below 0.5 Debye Units.

The invention is of particular importance in the production of shaped articles from polyacrylonitrile itself. It is however also of value in connection with copolymers, especially copolymers of acrylonitrile and another vinyl compound or compounds, in which the proportion of acrylonitrile exceeds 85%. Examples of vinyl compounds which may be copolymerised with acrylonitrile are methacrylonitrile, vinyl chloride, vinyl acetate, acrylic acid esters such as methyl and phenyl acrylate, styrene and its derivatives, and vinylidene chloride.

The coagulating medium is preferably a cyclic hydrocarbon free from olefinic and acetylenic unsaturation, and particularly good results are obtainable using one or more aromatic hydrocarbons such as benzene, toluene, xylene, or solvent naphtha. Other non-polar or nearly non-polar organic liquids free from olefinic and acetylenic unsaturation may however be used, for example, symmetrical halogenated hydrocarbons such as carbon tetrachloride and symmetrical tetrachlorethane. The non-polar or nearly non-polar liquid may if desired be employed in admixture with a smaller proportion of a polar liquid, e.g. an alcohol; for example benzene may be used in admixture with up to

about 25% of ethyl alcohol. Preferably the proportion of a polar liquid used is never so high as to form a separate phase.

Various solvents are available for forming solutions of the acrylonitrile polymers to be used in the process of the invention, including dimethyl formamide, gamma-butyrolactone, gamma- and delta-valerolactone, propiolactone and other beta-lactones, sulpholane (tetramethylene cyclic sulphone), nitroethanol or a nitropropanol (as described in Specification No. 690,553 of British Celanese Limited), cyclic aliphatic anhydrides such as maleic anhydride, succinic anhydride and glutaric anhydride, and solvent compositions comprising formic acid and/or nitromethane. Mixtures of two or more solvents may be used. Of these solvents we prefer to use dimethyl formamide or a composition containing as the major component nitromethane, formic acid or nitroethanol.

The concentration of the solution may, for example, be between 7.5% and 25%, and its temperature must be kept at least sufficiently high to ensure that the polymer does not begin to separate before extrusion or casting. Moreover, the temperature and the concentration should be correlated with the viscosity of the polymer to give a solution of satisfactory spinning or casting viscosity. For example, when a 20% solution in dimethyl formamide of a polyacrylonitrile of intrinsic viscosity below 12 is used, it is usually desirable to keep its temperature in the neighbourhood of 40° C. or higher. Other solutions may require yet higher temperatures to be maintained. The coagulating medium may be at or below room temperature, say at 10° to 20° C., or at a higher temperature. More rapid spinning can often be achieved by using a coagulating medium of suitable boiling point at a temperature between about 60° and 100° C. or even higher than by using it at room temperature.

The invention may be applied to the manufacture of films, and like shaped articles by extrusion or casting methods, but it is particularly important in connection with the manufacture of filaments from the acrylonitrile polymers. Such filaments may be made by extruding a solution of the polymer horizontally or vertically or at an angle to the horizontal into a bath of the desired coagulating medium, and the coagulating medium may for example be caused to flow in the same direction, in the opposite direction, or more or less transversely to the direction of travel of the filaments, or it may be in turbulent motion without flowing in any particular direction in contact with the filaments.

Filaments, films and like shaped articles made in accordance with the invention may be subjected to subsequent stretching, setting, and relaxing operations such as are known for filaments and films of polyacrylonitrile made by other methods. For example they may be stretched in hot water, e.g. water at a temperature between 80° and 100° C., or while softened by dry heat, e.g. while passing over a heated metal surface at a temperature of about 140° to 150° C. For example the filaments may be stretched to about 5, 10 or 15 times their original length and their tenacity considerably increased.

The stretched filaments and films may be "relaxed" in order to increase their extensibility, for example by heating them to about 140° to 150° C. in the absence of tension or under a tension insufficient to prevent them shrinking. Moreover, filaments and films made in accordance with the invention, whether or not they have been stretched, may be "set" by heating them to a temperature between 100° and 140° C. while they are held at constant length in order to increase their dimensional stability. For example, filaments may be heated while wound tightly on a bobbin.

The following examples illustrate the invention.

EXAMPLE I.

A 20% solution in dimethyl formamide of a polyacrylonitrile of intrinsic viscosity 6.3 was extruded in the form of filaments, while at a temperature of 40° C., into a coagulating bath of benzene or a 4:1 (by volume) mixture of benzene and ethyl alcohol at a temperature between 10° and 20° C. The filaments produced were of good strength and lustre.

EXAMPLE II.

A polyacrylonitrile of intrinsic viscosity 3.0 was dissolved in dimethyl formamide to give a solution of concentration 20%; the solution was kept at 70° C., and extruded at this temperature in the form of filaments into a coagulating bath of benzene at 10° to 20° C. The filaments obtained were passed over a heated metal surface at 140° to 150° C. and stretched to 12 times their original length. They were then heated to 140° C. in the absence of tension, whereupon they shrank to 85% of their stretched length. Before this relaxation operation, the stretched filaments had a tenacity of 2.2 gms. per denier, and an extension at break of 6%; after relaxation the tenacity was 2.0 gms. per denier and the extension at break was 12%.

EXAMPLE III.

A polyacrylonitrile of intrinsic viscosity 18.1 was dissolved in dimethyl formamide to give a solution of concentration 9%. The solution was kept at about 75° C., and was extruded in the form of filaments into a bath of toluene or tetrachlorethane at about the

same temperature. The filaments obtained could be stretched and relaxed by the methods described in Example II.

EXAMPLE IV.

A polyacrylonitrile of intrinsic viscosity about 8 was dissolved in aqueous formic acid at 120° C. and the solution cooled to 70° C. While at this temperature it was extruded in the form of filaments into a mixture of xylenes at about 95° C.

EXAMPLE V.

Polyacrylonitrile as used in Example IV was heated with nitromethane under pressure to 130° C., and sufficient water was then mixed in to give a mixture comprising 9 parts by volume of nitromethane and 1 part by volume of water. The solution of polyacrylonitrile so obtained was cooled to 85° C., and extruded in the form of filaments into a coagulating bath of xylene at about the same temperature. The filaments produced were at once stretched to 8 times their length while passing over a metal plate heated to 140° C., after which they were wound on a bobbin and the bobbin heated to 110° C. The product had a good tenacity and good dimensional stability.

EXAMPLE VI.

The process of Example V was repeated except that the polyacrylonitrile was dissolved in a mixture of 3 volumes of nitromethane to 1 volume of aqueous formic acid of concentration 85%.

EXAMPLE VII.

Polyacrylonitrile of intrinsic viscosity about 11 was heated with nitroethanol to 130° C. to give a solution of centration about 15%; the solution was cooled to 95° C., and at this temperature it was extruded in the form of filaments into a bath of toluene at the same temperature or into a bath of carbon tetrachloride at 50° C.

While the above examples all deal with the production of filaments from polyacrylonitrile, similar conditions can be used for the production of films and foils. The polyacrylonitrile can be replaced by another of the acrylonitrile polymers, especially a fibre-forming co-polymer of acrylonitrile and vinyl acetate or vinyl chloride containing 85% to 90% of acrylonitrile.

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